

# COATING COMPOSITION HAVING FLUORESCENT COLORANTS

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

[0001] The present invention relates to coating compositions containing fluorescent colorants, more particularly, to coating compositions containing reflective pigments and colorants which absorb visible light in a first wavelength band and produce fluorescent light at a second wavelength band when exposed to visible light.

### 2. Prior Art

[0002] Colored coating compositions typically include colorant particles dispersed in a resinous binder. The coating composition may further include reflective pigments, such as aluminum flake or metal oxide coated mica or other color effect pigment compositions or substrate-hiding materials, such as titanium dioxide. Conventional automotive solid-colored coatings include a resin and colored pigments which determine the desired coloration of the coating. Typically, solid color pigments are of a size such that they will scatter incident light effectively. The scattering will be in all directions.

[0003] Conventionally, in a pigmented coating composition, light that is scattered back out of the coating is described as being diffusely reflected while light that is scattered forwards through the coating composition is described as diffuse transmission. This scattering, in particular diffuse reflectance, is often desirable, providing opacity to the coating and hiding the surface of a coated article. Solid color pigments also typically absorb a portion of the incident light such that the light that is diffusely scattered and the remainder that is diffusely transmitted has a perceived color. Typically, this perceived color does not vary greatly with viewing angle. For those coating compositions that further include reflective pigments, such as aluminum flake or metal oxide coated mica or other color effect pigment compositions, the portion of the incident light that is not absorbed or diffusely reflected by the colored pigment will interact with these color effect pigments.

This portion of incident light may be specularly reflected by aluminum flake, or may interact with the coated mica or other effect pigment to produce a reflection whose perceived color is influenced by the structure of the pigment via an interference phenomenon. If this portion is specularly reflected by aluminum flake, there may be a perceived change in the color of the coating composition, typically described as flop. The perceived color will appear bright at viewing angles close to specular (on face), and appear to darken at viewing angles far from specular (on flop). If this portion undergoes interference on interaction with coated mica flake, there may also be a perceived change in the color of the coating composition, typically in hue as well as lightness or darkness. This viewing angle-dependent colored appearance of the coated surface produces color effects which are perceived positively by customers as being highly desirable, particularly as styling tools in automotive coatings.

[0004] Angle-dependent color effect pigments that result in hue changes (goniochromatic pigments) typically are interference pigments, such as mica pigments coated with a metal oxide. Interference pigments can be complex to prepare and are costly to include in a color effect coating composition.

[0005] Accordingly, a need remains for a coating composition having an angle-dependent color effect which may be produced cost effectively.

#### SUMMARY OF THE INVENTION

[0006] This need is met by the coating composition of the present invention which includes a resinous binder having dispersed therein colorants and reflective pigments. The colorants absorb visible light at a first wavelength band and produce fluorescent light at a second wavelength band when exposed to visible light. The colorants may be fluorescent dyes or fluorescent pigments. The color effect involves a balance between specularly reflected light, diffusely reflected light and fluorescence induced light. At angles close to the specular angle (on face) the reflected light is dominated by specular reflection and fluorescent induced light is not perceivable. At angles

far from specular (on flop) the observed light is dominated by the fluorescence of the colorant resulting in a different color from that seen on face. The fluorescence induced light is dependent on both the incident light source wavelength and intensity, hence the coating composition changes color as a function of time of day, weather conditions, and the like.

[0007] A complete understanding of the invention will be obtained from the following description when taken in connection with the accompanying drawing figures wherein like reference characters identify like parts throughout.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Fig. 1 is a cross-sectional view of one embodiment of a coated substrate of the present invention having colorants and reflective pigments;

[0009] Fig. 2 is another embodiment of a coated substrate of the present invention having an uncolored topcoat; and

[0010] Fig. 3 is another embodiment of a coated substrate of the present invention having the colorants and reflective pigments in separate layers and an uncolored topcoat.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] For purposes of the description hereinafter, the terms "upper", "lower", "right", "left", "vertical", "horizontal", "top", "bottom" and derivatives thereof shall relate to the invention as it is oriented in the drawing figures. However, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. It is also to be understood that the specific devices and processes illustrated in the attached drawings, and described in the following specification, are simply exemplary embodiments of the invention. Hence, specific dimensions and other physical characteristics related to the embodiments disclosed herein are not to be considered as limiting.

[0012] Various numerical ranges are disclosed in this patent application. Because these ranges are continuous, they include every value

between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

[0013] The present invention is depicted in Fig. 1 as including a coating 2 applied to a substrate 4. The coating 2 includes colorants 6 dispersed in a resinous binder along with platelet-like reflective pigments 8. As used herein, the visible spectrum includes wavelengths of about 400 nanometers (nm) to 700 nanometers (nm).

[0014] The embodiment shown in Fig. 2 includes a coating 20 having a layer 2 as described above as a basecoat and an uncolored polymeric composition as a top layer 22. The top layer 22 provides additional features to the coating 20, such as scratch resistance and the like. The resinous binders which are present in each of layers 2 and 22 may be the same or different from each other.

[0015] In another embodiment of the invention shown in Fig. 3, the colorants 6 and the reflective pigments 8 are present in distinct layers within a coating 30. The coating 30 includes a basecoat or lower layer 32 containing the reflective pigments, an upper layer 34 containing the colorants 6, and a top coat 22. The resinous binders which are present in each of layers 22, 32 and 34 may be the same or different from each other. In this embodiment, incident light has a high likelihood of striking colorants 6 in the layer 34 before reaching the reflective pigments 8 in the layer 32. In this manner, reflection of light passing through the colorants 6 but not absorbed thereby is maximized while the likelihood of visible light striking the reflected pigments 8 without having been partially absorbed by the colorants 6 is minimized. The colorants 6, the reflective pigments 8 and the resinous binder are described in turn hereinafter.

#### Colorants

[0016] The colorants of the present invention may be pigments or dyes which absorb visible light at a first wavelength band and produce fluorescent light at a second wavelength band when exposed to visible light. When polychromatic visible light strikes the colorants, a portion of the light is

absorbed by the colorants. The non-absorbed wavelengths are reflected by the reflective pigments included in the coating composition and exhibit a particular color, such as green or magenta. The absorbed wavelengths of light create an increased energy state in the colorants which is subsequently dissipated as fluorescent light in all directions from the colorants.

[0017] As shown in Fig. 1, the incident light I passes through a colorant particle 6. The incident light I is partially absorbed by the colorant 6. Light waves not absorbed by the colorant 6 are reflected by the reflective pigment 8 as a reflected light R. The energy of the wavelengths of light absorbed by the colorant 6 is dissipated in the form of fluorescent rays F in all directions away from the reflective pigment 8. A viewer of the coating sees one color on face from the specular reflection of the colorants 6 off the reflective pigments 8 (as rays R, only one being shown) and a different color on flop from the fluorescent light produced by the colorants 6 (as rays F). Although the fluorescent light F is present in all directions including on face, the reflected light R dominates on face and the fluorescent light F is not perceived.

[0018] Suitable materials for the colorants are dyes and pigments. Examples of dyes include acridines, anthraquinones, coumarins, diphenylmethanes, diphenylnaphylmethanes, quinolones, stilbenes, and triphenylmethanes.

[0019] The pigments may be inorganic or organic. Suitable organic pigments include azo (monoazo, disazo), naphthol, naphthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and polycyclic (phthalocyanine, quinacridone, perylene, perinone, diketopyrrolopyrrole, thioindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcationium, quinophthalone) pigments and mixtures thereof. The size of the pigment is selected so that the pigment particles will not scatter light effectively. Such scattering would induce significant diffuse reflectance that would be observed over a wide range of viewing angles. This would mask the fluorescence and diminish the change perceived in color with differing viewing angles.

[0020] A suitable primary particle size for the pigments is less than about 150 nm, or less than about 70 nm, or less than about 30 nm. The primary particles may be non-agglomerated. The dispersed particle size is the size of the individual particles (primary particles) or agglomerates of primary particles. Pigment particles may be prepared by milling bulk colorants, e.g., organic pigments, with milling media having a particle size of less than about 0.5 mm, or less than 0.3 mm or about 0.1 mm or smaller. The pigment particles are milled to nanoparticulate sizes in a high energy mill in an organic solvent system, such as butyl acetate using a dispersant, such as Solsperse® 32,500 available from Avecia, Inc. of Wilmington, Delaware, or in water using a dispersant, such as Solsperse® 27,000 available from Avecia, Inc. with an optional polymeric grinding resin. Other suitable methods of producing the colorants of the present invention include crystallization, precipitation, gas phase condensation and chemical attrition (i.e., partial dissolution).

Reflective Pigment

[0021] The coating composition of the present invention also includes reflective pigments 8. The reflective pigments may be in platelet form that include graphite, aluminum, metal oxide coated mica, metallic covered glass flake or other lustrous flake or other scattering members, such as described in U.S. Patent Application Serial No. 10/165,056, filed June 7, 2002, entitled "Use of Nanoparticulate Organic Pigments in Paint and Coatings", incorporated herein by reference.

Resinous Binder

[0022] The coating composition of the present invention includes a resinous binder. Conventional resinous binders may be used with the colorants described herein in automotive OEM compositions, automotive refinish compositions, industrial coatings, architectural coatings, electrocoatings, powder coatings, coil coatings and aerospace coatings.

[0023] Suitable resinous binders include a thermoplastic and thermosetting coating composition having components such as hydroxyl, carboxylic acid, carbamate, amide, or epoxy-containing acrylic copolymers

and hydroxyl, carboxylic acid, or carbamate-containing polyester polymers and oligomers, and isocyanate, hydroxyl, or carbamate-containing polyurethane polymers, or amine or isocyanate-containing polyureas which can enhance cure rate, appearance and other physical properties of the cured coating.

[0024] The acrylic polymers, if used, are typically copolymers of acrylic acid or methacrylic acid, hydroxyalkyl esters of acrylic or methacrylic acid such as hydroxyethyl methacrylate or hydroxypropyl acrylate, and/or carbamoyloxyethyl methacrylate, acrylamide or glycidyl methacrylate with one or more other polymerizable ethylenically unsaturated monomers such as alkyl esters of acrylic acid including methyl methacrylate and 2-ethyl hexyl acrylate, and vinyl aromatic compounds such as styrene, alpha-methyl styrene and vinyl toluene. The ratio of reactants and reaction conditions are selected to result in an acrylic polymer with pendant hydroxyl, carboxylic acid, carbamate, amide or epoxy functionality.

[0025] Besides acrylic polymers, the curable coating composition of the present invention can contain a polyester polymer or oligomer. Such polymers may be prepared in a known manner by condensation of polyhydric alcohols and polycarboxylic acids. Suitable polyhydric alcohols include ethylene glycol, neopentyl glycol, trimethylol propane and pentaerythritol.

[0026] Suitable polycarboxylic acids include adipic acid, 1,4-cyclohexyl dicarboxylic acid and hexahydrophthalic acid. Besides the polycarboxylic acids mentioned above, functional equivalents of the acids such as anhydrides where they exist or lower alkyl esters of the acids such as the methyl esters may be used. Also, small amounts of monocarboxylic acids such as stearic acid may be used.

[0027] Hydroxyl-containing polyester oligomers can be prepared by reacting an anhydride of a dicarboxylic acid such as hexahydrophthalic anhydride with a diol such as neopentyl glycol in a 1:2 molar ratio. Carbamate functionality can be introduced into the polyester by transcarbamylating with a material such as methyl carbinate.

[0028] Where it is desired to enhance air drying, suitable drying oil fatty acids may be used and include those derived from linseed oil, soya bean oil, tall oil, dehydrated castor oil or tung oil.

[0029] The polyesters are made to contain free terminal hydroxyl, carbamate and/or carboxyl groups that are available for further crosslinking reactions.

[0030] Polyurethane polymers containing terminal isocyanate or hydroxyl groups may also be used. The polyurethane polyols or NCO-terminated polyurethanes that can be used are those prepared by reacting polyols including polymeric polyols with polyisocyanates. The polyurea-containing terminal isocyanate or primary or secondary amine groups which can be used are those prepared by reacting polyamines including polymeric polyamines with polyisocyanates. The hydroxyl/isocyanate or amine/isocyanate equivalent ratio is adjusted and reaction conditions selected to obtain the desired terminal group. Examples of suitable polyisocyanates are those described in U.S. Patent No. 4,046,729 at col. 5, line 26 to col. 6, line 28, hereby incorporated by reference. Examples of suitable polyols are those described in U.S. Patent No. 4,046,729 at col. 7, line 52 to col. 10, line 35, hereby incorporated by reference. Examples of suitable polyamines are those described in U.S. Patent No. 4,046,729 at col. 6, line 61 to col. 7, line 32 and in U.S. Patent No. 3,799,854 at col. 3, lines 13 to 50, both hereby incorporated by reference.

[0031] Suitable curing agents for the curable coating composition include aminoplast resins and phenoplast resins and mixtures thereof, as curing agents for hydroxyl, carboxylic acid, amide and carbamate functional group containing materials. Examples of aminoplast and phenoplast resins suitable as curing agents in the curable compositions of the present invention are those described in U.S. Patent No. 3,919,351 at col. 5, line 22 to col. 6, line 25, hereby incorporated by reference.

[0032] Polyisocyanates and blocked polyisocyanates as curing agents for OH and primary and/or secondary amino group-containing materials are well known in the art. Examples of polyisocyanates and blocked isocyanates

suitable for use as curing agents in the curable compositions of the present invention are those described in U.S. Patent No. 4,546,045 at col. 5, lines 16-38; and in U.S. Patent No. 5,468,802 at col. 3, lines 48-60, both hereby incorporated by reference.

[0033] Anhydrides as curing agents for OH and primary and/or secondary amino group containing materials are well known in the art. Examples of anhydrides suitable for use as curing agents in the curable compositions of the present invention are those described in U.S. Patent No. 4,798,746 at col. 10, lines 16-50; and in U.S. Patent No. 4,732,790 at col. 3, lines 41 to 57, both hereby incorporated by reference.

[0034] Polyepoxides as curing agents for COOH functional group-containing materials are well known in the art. Examples of polyepoxides suitable for use as curing agents in the curable compositions of the present invention are those described in U.S. Patent No. 4,681,811 at col. 5, lines 33 to 58, hereby incorporated by reference.

[0035] Polyacids as curing agents for epoxy functional group-containing materials are well known in the art. Examples of polyacids suitable for use as curing agents in the curable compositions of the present invention are those described in U.S. Patent No. 4,681,811 at col. 6, line 45 to col. 9, line 54, hereby incorporated by reference.

[0036] Polyols, that is, material having an average of two or more hydroxyl groups per molecule, can be used as curing agents for NCO functional group containing materials and anhydrides and esters and are well known in the art. Examples of said polyols are those described in U.S. Patent No. 4,046,729 at col. 7, line 52 to col. 8, line 9; col. 8, line 29 to col. 9, line 66; and in U.S. Patent No. 3,919,315 at col. 2, line 64 to col. 3, line 33, both hereby incorporated by reference.

[0037] Polyamines can also be used as curing agents for NCO functional group containing materials and for carbonates and unhindered esters and are well known in the art. Examples of polyamines suitable for use as curing agents in the curable compositions of the present invention are

those described in U.S. Patent No. 4,046,729 at col. 6, line 61 to col. 7, line 26, hereby incorporated by reference.

[0038] The decorative and protective coating composition may be used as a single coating, as a clear top coating composition, as a base coating in a two-layered system, as layers of a multi-layered system including a clear top coating composition, colorant layer and base coating composition, or as a primer layer.

[0039] The concentration of the colorants in the coating composition is about 0.001 wt.% to about 50 wt.% or about 0.001 wt.% to about 20 wt.%. The concentration of the reflective pigments in the coating composition is about 0.1 wt.% to about 50 wt.%.

[0040] The invention is further described by reference to the following examples.

#### EXAMPLES

[0041] Examples 1-9 describe the production of coating compositions of the present invention containing colorants with and without reflective pigments.

[0042] Examples 10-20 describe coated articles using the compositions of Examples 1-9. Example 15 corresponds to the embodiment of Fig. 1. Examples 10, 11, 16 and 17 correspond to the embodiment of Fig. 2. Examples 12, 18 and 19 correspond to the embodiment of Fig. 3.

[0043] Examples 13, 14 and 20 are comparatives.

#### Example 1

[0044] An 11.10g dispersion of Pigment Yellow 139 milled to nanoparticulate size using a high energy mill with a milling media of about 0.1 mm, was blended with 37.76g of aluminum flake toner D769 available from PPG Industries, Pittsburgh, PA and 51.13g of solvent reducer package D871 available from PPG Industries, Pittsburgh, PA.

### **Example 2**

[0045] A 17.92g dispersion of Pigment Yellow 128 milled to nanoparticulate size using a high energy mill with a milling media of about 0.1 mm, was blended with 34.87g of aluminum flake toner D769 and 47.21g of solvent reducer package D871.

### **Example 3**

[0046] A 6.35g dispersion of Pigment Yellow 139, milled to nanoparticulate size using a high energy mill with a milling media of about 0.1 mm, was blended with 62.30g of resinous clear coat binder Concept® DCU2042 available from PPG Industries, Pittsburgh, PA, 17.69g isocyanate hardener DCX61 hardener available from PPG Industries, Pittsburgh, PA and 13.66g of solvent reducer package D870 Reducer available from PPG Industries, Pittsburgh, PA.

### **Example 4**

[0047] A 10.74g dispersion of Pigment Yellow 128 milled to nanoparticulate size using a high energy mill with a milling media of about 0.1 mm, was blended with 59.39g of resinous clear coat binder Concept® DCU2042, 16.86g isocyanate hardener DCX61 and 13.02g of solvent reducer package D870.

### **Example 5**

[0048] A 9.35g dispersion of Pigment Yellow 139 milled to nanoparticulate size using a high energy mill with a milling media of about 0.1 mm, was blended with 40.42g of aluminum flake toner Concept® DMC982 available from PPG Industries, Pittsburgh, PA, 4.95g resinous clearcoat binder Concept® DCU2042, 12.22g acetone, 12.98g solvent reducer package D870, and 20.08g isocyanate hardener DCX61.

### Example 6

[0049] A 10g solution of Rhodamine 6G (0.2% by weight in methanol, available from Aldrich Chemical Co., Inc., Milwaukee, WI,) was blended with 40.00g of aluminum flake toner D769 and 50g of solvent reducer package D871.

### Example 7

[0050] A 10g solution of oxazine-4-perchlorate (0.2% by weight in methanol, available from Fisher Scientific, Pittsburgh, PA) was blended with 40.00g of aluminum flake toner D769 and 50g of solvent reducer package D871.

### Example 8

[0051] A 4g solution of Rhodamine 6G was blended with 63g of resinous clear coat binder Concept® DCU2042, 18g isocyanate hardener DCX61 and 15g of solvent reducer package D870.

### Example 9

[0052] A 4g solution of oxazine-4-perchlorate was blended with 63g of resinous clear coat binder Concept® DCU2042, 18g isocyanate hardener DCX61 and 15g of solvent reducer package D870.

### Example 10

[0053] The coating composition of Example 1 was spray applied to a substrate as a basecoat. After a 30-minute dry time under ambient conditions, the coated substrate was further sprayed with a two-component protective clearcoat containing a blend of resinous clearcoat binder Concept® DCU2042, solvent reducer package D870, and isocyanate hardener DCX61 mixed according to the supplier's recommendations. After a further 60 minutes of dry time, the coated article was baked for 1 hour at 60°C. After the bake period, the coated article was inspected visually. When viewed at high angles close to normal incidence, the article appeared to be orange in color

with a metallic luster. However, when viewed at shallow angles, the color changed to a yellowish green and showed less metallic luster.

#### Example 11

[0054] The process of Example 10 was followed using the composition of Example 2 instead of the composition of Example 1 as the basecoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be yellow in color with a metallic luster. However, when viewed at shallow angles, the color changed to a green and showed less metallic luster.

#### Example 12

[0055] The coating composition of Example 4 was spray applied as a tinted clearcoat over a silver metallic basecoat. After a 30-minute dry time under ambient conditions, the coated substrate was further sprayed with a two component protective clearcoat containing a blend of resinous clearcoat binder Concept® DCU2042, solvent reducer package D870, and isocyanate hardener DCX61 mixed according to the supplier's recommendations. After a further 60 minutes of dry time, the coated article was baked for 1 hour at 60°C. After the bake period the coated article was inspected visually. When viewed at high angles close to normal incidence, the article appeared to be yellow in color with a metallic luster. However, when viewed at shallow angles, the color changed to a green and showed less metallic luster.

#### Comparative Example 13

[0056] The process of Example 12 was performed except that a white basecoat was used instead of a silver metallic basecoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be yellow in color. When viewed at shallow angles, the article also appeared to be yellow in color. No color effect was evident.

#### Comparative Example 14

[0057] The process of Example 13 was followed using the composition of Example 3 instead of the composition of Example 4 as the tinted clearcoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be orange in color. When viewed at shallow angles, the article also appeared to be orange in color. No color effect was evident.

#### Example 15

[0058] The coating composition of Example 5 was spray applied to a suitable substrate as a direct gloss monocoat. After 60 minutes of dry time, the coated article was baked for 1 hour at 60°C. After the bake period the coated article was inspected visually. When viewed at high angles close to normal incidence, the article appeared to be orange in color with a metallic luster. However, when viewed at shallow angles, the color changed to a green and showed less metallic luster.

#### Example 16

[0059] The process of Example 10 was followed using the composition of Example 6 instead of the composition of Example 1 as the basecoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be magenta in color with a metallic luster. However, when viewed at shallow angles, the color changed to orange and showed less metallic luster.

#### Example 17

[0060] The process of Example 10 was followed using the composition of Example 7 instead of the composition of Example 1 as the basecoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be blue in color with a metallic luster. However, when viewed at shallow angles, the color changed to red and showed less metallic luster.

### Example 18

[0061] The process of Example 12 was followed using the composition of Example 8 instead of the composition of Example 4 as the tinted clearcoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be magenta in color with a metallic luster. However, when viewed at shallow angles, the color changed to orange and showed less metallic luster.

### Example 19

[0062] The process of Example 12 was followed using the composition of Example 9 instead of the composition of Example 4 as the tinted clearcoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be blue in color with a metallic luster. However, when viewed at shallow angles, the color changed to a red and showed less metallic luster.

### Comparative Example 20

[0063] The process of Example 18 was performed except that a white basecoat was used instead of a silver metallic basecoat and visually inspected. When viewed at high angles close to normal incidence, the article appeared to be magenta in color. When viewed at shallow angles, the article also appeared to be magenta in color. No color effect was evident.

[0064] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.